Europäisches Patentamt

**European Patent Office**

**Office européen des brevets**

⑪ Publication number: **0 130 073**
**A2**

⑫ **EUROPEAN PATENT APPLICATION**

㉑ Application number: **84304276.3**

㉒ Date of filing: **25.06.84**

㉕ Int. Cl.⁴: **H 01 M 6/14**

⑪ Applicant: **Standard Oil Company**
**200 East Randolph Drive**
**Chicago Illinois 60601(US)**

㉒ Inventor: **Connolly, John Francis**
**625 Lake Road**
**Glen Ellyn Illinois 60137(US)**

㉒ Inventor: **Thrash, Robert James**
**571 Iroquois Trail**
**Carol Stream Illinois 60188(US)**

㉔ Representative: **Laredo, Jack Joseph et al,**
**Elkington and Fife High Holborn House 52/54 High**
**Holborn**
**London, WC1V 6SH(GB)**

�54 **A method of enhancing and controlling the solubility of lithium salts in liquid sulfur dioxide.**

� The solubility of lithium salts in sulfur dioxide-based solvent systems is enchanced and controlled by the presence of a salt which contains a cation selected from the group consisting of metal cation complexes, quaternary ammonium cations and organic phosphonium cations.

EP 0 130 073 A2

A METHOD OF ENHANCING AND CONTROLLING THE
SOLUBILITY OF LITHIUM SALTS IN LIQUID SULFUR DIOXIDE

## Background of the Invention

### Field of the Invention

This invention relates to a method of enhancing and
controlling the solubility of a lithium salt in liquid
sulfur dioxide.  More particularly, the invention relates
to a method of increasing the solubility of lithium salts
in a sulfur dioxide-based solvent system, which method
involves the addition of a solubility-enhancing additive
comprising a salt which contains at least one cation
selected from the group consisting of metal cation complexes,
quaternary ammonium cations and organic phosphonium
cations.

### Description of the Prior Art

Recently, much effort has been expended in the
development of ambient temperature, high energy density
cell systems which provide both higher voltages and higher
total capacities (volumetric and gravimetric) than those
of the known Leclanche or alkaline cells having zinc anodes.
The high energy density cell systems are centered around
the use of active metals (metals above hydrogen in the
EMF series which are unstable in aqueous environments)
as anodes in non-aqueous solution cells.  As used herein,
"non-aqueous" is intended to mean substantially anhydrous.

The need for high energy output with low weight
requires the use as the electrodes of active metals and,
in particular, active metals having low equivalent weights.
The alkali metals qualify in these respects.  However,
since the alkali metals are generally reactive in electrolyte
systems containing water, acids, alcohols, or other proton-
donating solvents, these liquids must be replaced by

solvents incapable of undergoing protolytic reactions with
such metals.  A continuing problem in the choice of such
solvents is the tendency to co-reduction of said solvents
during the reduction of alkali metal ions to the free
5    metal.  Thus, it will readily be apparent that not only
must the solvent be  miscible with, and promote, the
electrical conductivity of the supporting electrolyte
salt, but it must also remain substantially chemically
inert to the electrodes and electrolyte during storage
10   as well as during operation of the electrochemical system.
In like manner, the electrolyte must be chemically inert
with respect to the electrodes.

Various cell systems have been developed utilizing
lithium as the anode electrode material.  Those showing
15   promise in the terms of voltage stability and high
discharge capability have fluid cathode depolarizers which
also generally·serve the function of a supporting
electrolyte salt solvent.  When a cell of this type is
not being discharged, the fluid depolarizer/supporting
20   electrolyte solution reacts with the anode metal to a
limited extent with a protective film coating being formed
on the surface of the anode.  Full reaction between the
anode and the fluid depolarizer with which it is in contact
is thereby substantially prevented and cell self-discharge
25   is limited.

To date, the active metal battery art has uniformly
emphasized the necessity for soluble anode products and
insoluble cathode products during discharge, and the con-
comitant need to facilitate anodic (active metal) ion
30   transport through the electrolyte to the cathode or posi-
tive electrode current collector.  As recognized in the
art, such systems employ anodes which are termed electrodes
of the first kind.  These are understood to be electrodes
in which the potential-determining ion in solution is
35   not in equilibrium with a solid salt phase.  Such cells
are characterized by cell solutions which are unsaturated
in the electrode (or potential-determining) ion, thereby

allowing the concentration of the potential determining ion to be varied at will. As used in the art, such cells are further characterized by: (a) very high (although below saturation) concentrations of the anode ion; (b) soluble discharge products at the anode; and (c) high ion transfer in solution from anode to positive electrode.

For example, Gabano (U.S. Patent No. 3,511,716) discloses a cell in which oxidized lithium goes into solution during discharge and migrates toward the positive electrode. Gabano emphasizes that the solubility of lithium in the solution must be as high as possible to achieve adequate transfer of lithium ions to the positive electrode. Similarly, Skarstad et al. (U.S. Patent No. 4,246,327) discusses $SO_2-$ and $SOCl_2$-based batteries which make use of lithium ion transport and deposit lithium salts as insoluble discharge products on a high surface area cathode.

More specifically, the art has taught that soluble anode products coupled with insoluble cathode products are required and necessary in active metal secondary batteries. Maricle et al. (U.S. Patent No. 3,567,515), for example, simply state: "As a general rule, insoluble [cathode] products are obtained when alkali-metal electrolytes are employed ....". In addition, Maricle et al. expressly teach that soluble cathode products are not preferred, especially in secondary batteries.

An even more sweeping generalization is found in Eisenberg, "Study of the Secondary lithium Electrode in Organic Electrolyte", Final Report on LBL Subcontract 4507210, April 1981. Eisenberg teaches (at page 19) that, for a lithium anode in organic, aprotic electrolyte systems, high solubility of lithium ion salts is necessary to provide for the necessary ionic transport through the electrolyte. In such systems, Eisenberg concludes that

"....the solubility of the lithium anode product in the electrolyte appears to be an unavoidable _fact of life_." (emphasis in original).

Though the art has thus concentrated exclusively
5    upon active metal anodes of the first kind, the hoped-
for advantages of greater conversion of the active metal,
higher effective current density and improved low tempera-
ture behaviour have not been realised in practice.
Instead, a range of problems has plagued virtually all
10   systems employing an active metal anode of the first kind.
One such problem results from difficulties in obtaining
requisite ionic transport to and from each electrode.
During each charging operation, the active material must
be transported from within the solution to the surface
15   of the anode base plate. On the other hand, during each
discharge the deposited layers must be completely redis-
solved. Maintaining uniform current distribution and
adequate convection in the electrolyte is thus very
important with this type of battery. If uniformity
20   of current distribution is inadequate, several problems
arise, namely:

(1) local problems: formation of dendrites and
nodules on the surface of the anode;

(2) asymmetrical deposition of the active materials
25   along the electrode surface (shape change); and

(3) asymmetrical deposition of active materials
in the positive electrode.

Additional problems arise from the partially irre-
versible behaviour of the active deposits. As a result
30   of the asymmetry between current efficiencies for deposi-
tion and dissolution, and as a result of asymmetry in
respect of corrosion processes, the active deposits show
a partially irreversible behaviour. Dendrite formation
in cells with anodes of the first kind and the attendant
35   problems are discussed in Beck et al. (U.S. Patent

No. 4,119,767), by Koch (U.S. Patent No. 4,252,876), and by Schlaikjer (U.S. Patent No. 4,139,680). Beck et al. and Koch also encountered shape change or morphology problems. The disadvantages of irreversible asymmetrical

5   deposits clogging the cathode are discussed by Beck et al. (supra) Fraioli et al. (U.S. Patent No. 3,551,205) and Maricle et al. (Supra).

In general, attempts to solve such problems associated with an active metal anode of the first kind have

10   centered on (1) electrolyte-solvent combinations such as those taught by Gabano et al.; Skarstad et al.; and Eisenberg (U.S. Patent No. 3,891,458, reissued as Re. 30,661); (2) additives to help dendrite dissolution such as the teachings of Beck et al.; and (3) high surface

15   area cathodes such as those discussed by Maricle et al. and Fraioli et·al.

To the best of our knowledge, no complete solution to the difficulties inherent in active metal anodes of the first kind has yet been found. This failure has

20   prevented the development of an active metal secondary battery which is lightweight, provides stable voltage at open circuit, is operable at ambient temperatures, has a large energy density, and can be reliably cycled through numerous charge/discharge cycles. A need therefore

25   exists for a secondary battery with the desirable charac-teristics expected of an active metal-based electrochemical cell, but without the present disadvantages.

## Summary of the Invention

The present invention is directed to the discovery

30   of a method for increasing the solubility of lithium salts in a sulfur dioxide-based solvent system which involves the addition of a solubility-enhancing additive comprising a salt which contains at least one cation selected from the group consisting of metal cation

35   complexes, quaternary ammonium cations and organic phosphonium cations.

One embodiment of the invention is a method for
modifying the solubility of a lithium salt in a non-
aqueous solvent system which comprises dissolving said
lithium salt and a solubility-modifying additive in the
solvent system, wherein said solvent system comprises
a major portion of sulfur dioxide, the amount of said
lithium salt is in excess of the amount which is soluble
in the solvent system in the absence of said solubility-
modifying additive, the amount of said solubility-modi-
fying additive is effective to increase the solubility
of the lithium salt, and said solubility-modifying additive
comprises a salt which contains at least one cation
selected from the group consisting of metal cation
complexes, quaternary ammonium cations and organic
phosphonium cations.

Another embodiment of the invention is the composition
prepared by the process which comprises dissolving a
lithium salt and a solubility-modifying additive in a
non-aqueous solvent system the  solvent system comprising
a major proportion of sulfur dioxide, the amount of the
lithium salt being in excess of the amount which is
soluble in the solvent system in the absence of the
solubility-modifying additive, the amount of the solubility-
modifying additive being effective to increase the
solubility of the lithium salt, and the solubility modifying
additive comprising a salt which contains at least one
cation selected from the group consisting of metal cation
complexes, quaternary ammonium cations and organic
phosphonium cations.

A further embodiment of the invention is an electro-
chemical cell comprising:  (a) a lithium anode; (b) a
positive electrode current collector; and (c) an electro-
lyte which comprises the above-described composition.

An object of this invention is to provide a method
for controlling the solubility of lithium salts in liquid
sulfur dioxide.

Another object of this invention is to provide an improved electrolyte for use in primary and secondary electrochemical cells which utilize lithium electrodes.

Another object of this invention is to provide an improved rechargeable, non-aqueous, ambient temperature electrochemical cell which utilizes a lithium electrode.

A further object of this invention is to provide a method for control of the lithium salt concentration in a sulfur dioxide-based electrolyte solution for use in an electrochemical cell having a lithium electrode.

## Detailed Description of the Invention

We have found that the solubility of lithium salts in a sulfur dioxide-based solvent system can be enhanced in a controlled manner and over a broad range through the addition of a solubility-enhancing additive which comprises a salt containing at least one cation selected from the group consisting of metal cation complexes, quaternary ammonium cations and organic phosphonium cations.

In the practice of this invention, a liquid non-aqueous solvent system is used which comprises a major pro-portion of sulfur dioxide. Suitable solvent systems include substantially pure liquid sulfur dioxide and mixtures which consist of a minor proportion of one or more cosolvents in combination with a major proportion of sulfur dioxide. However, the use of substantially pure sulfur dioxide is generally preferred.

Suitable cosolvents which can be combined with sulfur dioxide in the practice of this invention are liquid organic and inorganic compounds which lack acidic hydrogen atoms and contain one or more atoms having at least one unshared pair of electrons. For the purposes hereof, "acidic hydrogen atoms" are those which are capable of being abstracted by lithium metal. However, strongly basic cosolvents such as amines are not generally desirable.

More specifically, suitable cosolvents are organic
or inorganic liquids which contain at least one element
which is selected from Groups 3a, 4a, 5a and 6a of the
Periodic Table [Handbook of Chemistry and Physics, 57th

5    ed. (1976-77), p. B-4]. Preferred elements from this
group include, for example, boron, silicon, nitrogen,
phosphorus, oxygen and sulfur as well as combinations
of these elements. Organic solvents which contain two
or more atoms of such elements in each molecule are

10   particularly suitable.

Preferred liquid organic compounds for use as a
cosolvent in the practice of this invention include, but
are not limited to, trialkyl borates, boronic acid esters,
borinic acid esters, tetraalkyl silicates, alkylalkoxy-

15   silanes, nitroalkanes, alkylnitriles, dialkyl-amides,
lactams, tetraalkyl ureas, acetals, ketals, mono-carboxylic
acid esters, orthoesters, lactones, dialkyl carbonates
alkylene carbonates, orthocarbonates, monoethers, polyethers,
monocarboxylic acid anhydrides, dialkyl sulfates, dialkyl

20   sulfites, alkylene sulfites and sulfones. Specific
examples include triethyl borate, diethyl methylboronate,
methyl diethylborinate, tetramethyl silicate, trimethoxy-
methylsilane, nitroethane, acetonitrile, dimethylformamide,
1-methyl-2-pyrrolidinone, tetramethylurea, 1,1-diethoxy-

25   ethane, 2-2-dimethoxypropane, ethyl acetate, trimethyl
orthoformate, $\gamma$-butyrolactone, dimethyl carbonate, ethylene
carbonate, tetramethyl orthocarbonate, diethyl ether,
tetrahydrofuran, ethylene glycol, dimethyl ether, acetic
anhydride, dimethyl sulfate, dimethyl sufite, ethylene

30   sulfite and tetramethylene sulfone.

Preferred liquid inorganic compounds for use as
cosolvents in the practice of this invention include,
but are not limited to, phosphorus oxychloride, thionyl
chloride and sulfuryl chloride. Thionyl chloride is

35   particularly preferred.

The solubility-modifying additive for use in the practice of this invention comprises one or more salts which contain at least one cation selected from the group consisting of metal cation complexes, quaternary ammonium cations and organic phosphonium cations. Preferred solubility-modifying additives contain at least one anion selected from the group consisting of perchlorate, tetra-fluoroborate, hexafluorophosphate, dithionite, sulfate, phosphate, chloride, bromide, iodide and fluoride. Preferred metal cation complexes are metal cations which are associated with one or more organic ligands of chelating agents. It will be appreciated, of course, that such coordinated or chlated metal cations should be free of acidic hydrogen atoms. Examples of suitable metal cation complexes include, but are not limited to, complexes of an alkali metal cation with a crown ether, such as $Na(15\text{-crown-5})^+$ complexes of an alkali metal cation with a cryptand, such as $K(C_{18}H_{36}N_2O_6)^+$, $[Co(8\text{-hydroxyquinoline})_2(NH_3)_2]^+$,

$[Co(8\text{-hydroxyquinoline})_2(2,2'\text{-dipyridyl})]^+$, $Mn(2,2'\text{-dipyridyl})_3^{++}$, and $Mn(1,10\text{-phenanthroline})_3^{++}$. Of these examples, $Mn(2,2'\text{-dipyridyl})_3^{++}$ and $Mn(1,10\text{-phenanthroline})_3^{++}$ are particularly preferred.

Quaternary ammonium salts are highly suitable for use as the solubility-modifying additive in the practice of this invention. Preferred quaternary ammonium salts are of the formula:
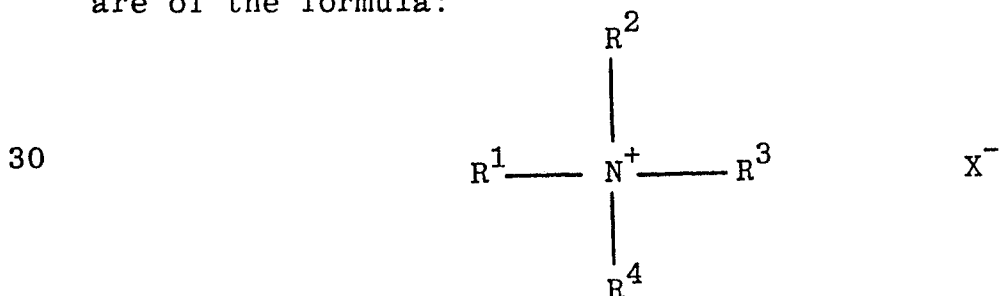
$$R^1 - \overset{\overset{\displaystyle R^2}{\displaystyle |}}{\underset{\underset{\displaystyle R^4}{\displaystyle |}}{N^+}} - R^3 \qquad\qquad X^-$$

wherein $R^1$, $R^2$, $R^3$ and $R^4$ are independently selected from the group consisting of hydrocarbyl groups containing from 1 to 20 carbon atoms, and $X^-$ is selected from the group consisting of perchlorate, tetrafluoroborate, hexafluorophosphate, dithionite, sulfate, phosphate, chloride, bromide, iodide and fluoride. More preferably, $R^1$, $R^2$, $R^3$ and $R^4$ are independently selected from the group consisting of alkyl groups having from 1 to 10 carbon atoms, and $X^-$ is selected from the group consisting of perchlorate, tetrafluoroborate, hexafluorophosphate, dithionite and sulfate. Examples of suitable quaternary ammonium salts include tetrabutylammonium perchlorate, tetrahexylammonium perchlorate, tetramethylammonium tetrafluoroborate and tetrapropylammonium hexafluorophosphate.

Phosphonium salts which are suitable for use as the solubility-modifying additive in the practice of this invention are of the formula.
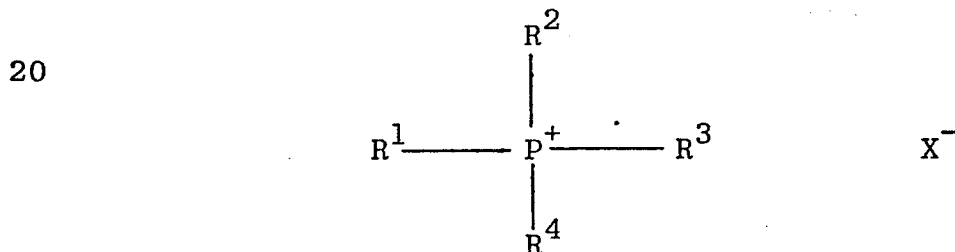
$$R^1 \longrightarrow \overset{\displaystyle R^2}{\underset{\displaystyle R^4}{\overset{|}{\underset{|}{P^+}}}} \longrightarrow R^3 \qquad X^-$$

wherein $R^1$, $R^2$, $R^3$ and $R^4$ are independently selected from the group consisting of hydrocarbyl groups containing from 1 to 20 carbon atoms, and $X^-$ is selected from the group consisting of perchlorate, tetrafluoroborate, hexafluorophosphate, dithionite, sulfate, phosphate, chloride, bromide, iodide and fluoride. More preferably, $R^1$, $R^2$, $R^3$ and $R^4$ are independently selected from the group consisting of alkyl groups of from 1 to 10 carbon atoms, and aryl and alkyl-substituted aryl groups of from 6 to 12 carbon atoms; and $X^-$ is selected from the group consisting of perchlorate, tetrafluoroborate,

hexafluorophosphate, dithionite and sulfate. Examples of
suitable phosphonium salts include tetrabutylphosphonium
tetrafluoroborate, tetraphenylphosphonium perchlorate and
tetraphenylphosphonium hexafluorophosphate.

5      The solubility-modifying additive of this invention
desirably has a solubility in the sulfur dioxide-based
solvent system of this invention at the temperature and
pressure of use of at least 0.001 equivalent per liter,
preferably of at least 0.01 equivalent per liter, and,

10     more preferably, of at least 0.1 equivalent per liter.
As used herein, equivalents are calculated on the basis
of a salt's ability to provide lithium cations, and the
ability of non-lithium salts to combine with lithium
cations on the basis of formal charge. For example, one

15     mole of $Li_2SO_4$ is equal to two equivalents (two $Li^+$ cations
per molecule), and one mole of $LiClO_4$ is equal to one
equivalent (one $Li^+$ cation per molecule). Similarly,
one mole of $Mn(1,10\text{-phenanthroline})_3(ClO_4)_2$ is equal to
two equivalents (two $ClO_4^-$ anions per molecule), and one

20     mole of tetramethylammonium tetrafluoroborate is equal
to one equivalent (one $BF_4^-$ anion per molecule).
       In the practice of this invention, the solubility-
modifying additive is used in an amount which is effective
to increase the solubility of a lithium salt in a non-

25     aqueous solvent system which comprises a major proportion
of sulfur dioxide. Preferably, the amount of the solubi-
lity-modifying additive is effective at least to double
the solubility of the lithium salt in the solvent system.
The use of one equivalent of solubility-modifying

30     additive in accordance with this invention can, in some
cases, increase the solubility of a lithium salt in
substantially pure sulfur dioxide by as much as a factor
of 200 or more even when they share a common anion (see
Example 1 below).

35

Any lithium salt which does not react with the solvent system is suitable for use in the practice of this invention. However, lithium perchlorate, lithium dithionite, lithium sulfate, lithium tetrafluoroborate and lithium hexafluorophosphate are particularly preferred.

We have found that the method of this invention for enhancing the solubility of lithium salts in a sulfur dioxide-based solvent system is particularly useful for generating electrolytes for use in electrochemical cells which utilize an anode which comprises lithium. Such electrolytes are especially useful in an ambient temperature rechargeable electrochemical cell which utilizes a lithium anode as an electrode of the second kind. Generally, electrodes of the second kind are considered to be those in which the potential-determining ion in solution is in equilibrium with a solid salt phase. The activity and concentration of the potential-determining ion in solution is controlled by this equilibrium.

An electrolyte prepared in accordance with the method of this invention is particularly well suited for use in an electrochemical cell having a lithium electrode of the second kind of the type which is set forth in copending U.S. Patent Application Serial No. 471,429 (filed March 2, 1983). This copending application is directed to a rechargeable non-aqueous electrochemical cell which comprises a lithium anode, a cathode depolarizer, a positive electrode current collector, and an electrolyte comprising an ionizing solvent, a lithium salt and a supporting electrolyte salt comprising at least one component of the general form $R^+X^-$, wherein $R^+$ is a cation other than that of lithium, and $X^-$ is an anion which forms a lithium salt which is less soluble in the cell than $R^+X^-$, and wherein the saturated concentration of lithium cation in the electrolyte is between $10^{-9}$ and $10^{-1}$ equivalents per liter. Although the lithium cation concentration

in the electrolyte of such a cell may vary over a wide
range, optimum cell performance requires that the lithium
cation concentration be optimized.  Unfortunately,
optimization of the lithium cation concentration in the
electrolyte solution of such a cell has been very
difficult in the past.

As used herein, the term "supporting electrolyte
salt" refers to the primary conducting component in the
electrolyte acting as the principal current carrier.
While other conducting salts can be present, the supporting
electrolyte salt is present in the highest concentration.
Moreover, salts which have saturated concentrations
between $10^{-9}$ and $10^{-1}$ equivalents per liter in the cell
solution are referred to herein as "slightly soluble"
salts.  It should be understood that the generic
representation·of ions (e.g. as $R^+$ or $X^-$) refers to ions
which can carry one or more positive or negative charges
and is not intended, therefore, to denote only singly
charged ions.  References to cation solubility herein
are, generally speaking, references to the solubility
of salts containing the cation.

The present invention provides a highly satisfactory
method for the control of lithium salt solubility over
a wide range of concentrations in a non-aqueous solvent
system which comprises a major proportion of sulfur dioxide.
In addition, such a solvent system is particularly satis-
factory for use in an electrochemical cell of the type
described above, since sulfur dioxide has the ability
to form a passivating (yet ion conducting) film on lithium
electrodes.  Also advantageous is the fact that sulfur
dioxide can perform the dual function of both solvent
and cathode depolarizer.  Thus, liquid sulfur dioxide
is a highly efficacious electrolyte component.  It will
be appreciated, of course, that a cathode depolarizer
is an electrochemical couple in which the oxidized form
is reversibly reducible at the positive electrode;

$SO_2/S_2O_4^=$ represents such a couple. During discharge,
the depolarizer is reduced at the positive electrode,
and the process is reversed when the cell is charged.
The $SO_2/S_2O_4^=$ couple is particularly satisfactory since
the reduced form of the couple is soluble in a sulfur
dioxide-based solvent system. Such a system obviates
any need for ultrahigh suface area positive electrodes.

As noted above, an electrolyte prepared in accordance
with the method of this invention is particularly suitable
for use in a rechargeable electrochemical cell having
a lithium electrode of the second kind. Upon discharge,
lithium cations ($Li^+$) are ejected from the anode and
combine with anions ($X^-$) already present in relatively
high concentration in the electrolyte solution, to form
a slightly soluble lithium salt ($Li^+X^-$) which then
precipitates onto the anode. At the positive electrode,
the cathode depolarizer is reduced to a product which
can be either soluble or insoluble in the electrolyte
solution. When the cell is recharged, the slightly
soluble lithium salt on the anode ($Li^+X^-$) is removed with
the anion going back into solution and the lithium cations
($Li^+$) being reduced back to the metal at the anode. At
the positive electrode, the reduction product is oxidized
back to the original state of the cathode depolarizer.

Supporting electrolyte salts which are useful in
an electrolyte solution for use in an electrochemical
cell in accordance with this invention generally having
a high conductivity in the electrolyte solvent system
and, preferably, should be highly soluble. In addition,
the electrolyte salt should also be substantially stable
with respect to the other cell components. It will be
appreciated, of course, that the solubility-modifying
additive of this invention can be utilized as the supporting
electrolyte salt.

Suitable supporting electrolyte salts are of the general form $R^+X^-$ wherein the salt does not have any acidic hydrogen atoms which are capable of being abstracted by lithium metal. The cationic component, $R^+$, is a cation other than that of lithium and is preferably selected from the group consisting of metal cation complexes, quaternary ammonium cations and organic phosphonium cations. Any of the cations which are suitable components of the previously defined solubility-modifying additive are suitable for use as $R^+$.

The anionic component $X^-$ of said supporting electrolyte salt comprises any anion which combines with $Li^+$ to form a slightly soluble lithium salt, $Li^+X^-$, which is less soluble than $R^+X^-$ in the electrolyte solvent system and is stable at the positive electrode (except in those cases wherein the anion is the same as the reduction product formed at the positive electrode during discharge, such as $S_2O_4^=$ produced by production of $SO_2$). Suitable anions can be selected from the group consisting of halide, trihalide and oxyhalide anions; oxyacid, halide and organic anions of elements which are selected from Groups 3a, 4a, 5a and 6a of the Periodic Table [Handbook of Chemistry and Physics, 57th ed. (1976-77), p. B-4]; and anionic complexes of transition and rare earth metals. Examples of suitable anions include, but are not limited to, perchlorate, dithionite, sulfate, fluoride, phosphate, tetrafluoroborate, and hexafluorophosphate. Perchlorate and dithionite ions are particularly preferred.

The supporting electrolyte salt should be sufficiently soluble in the electrolyte solvent system to produce a concentration which is within the range of from 0.01 to 5.0 equivalents per liter, and preferably within the range of from 0.01 to 4.0 equivalents per liter. For the preferred supporting electrolyte salts, this corresponds to molar concentrations of from 0.005 molar to 5.0 molar, and preferably, from 0.005 molar to 4.0 molar.

The electrolyte solution for use in an electrochemical cell in accordance with this invention is preferably saturated with respect to lithium cations. One method of achieving $Li^+$ saturation or near saturation in solutions comprising a non-aqueous sulfur dioxide-based solvent system, at least one supporting electrolyte salt, and the solubility-modifying additive of this invention involves adding the required amount of one or more lithium salts to the otherwise complete electrolyte solution. However, it will be appreciated that the various electrolyte solution components can be combined in any desired sequence.

In a rechargeable electrochemical cell having a lithium anode of the second kind, a high lithium cation concentration in the electrolyte solution can result in an asymmetric deposition of the anode metal during charge. Therefore, the electrolyte solution should be saturated with respect to lithium cations, but the concentration of lithium cations should also be as small as possible consistent with desirable current densities. Preferred concentration ranges can be estimated by considering planar and porous electrodes at practical charging densities. If a planar anode with a discharge product deposited on its surface is assumed, in order that a charging current density of substantially 50 $mA/cm^2$ should be achieved, the lithium cation concentration should be substantially $10^{-1}$ equivalent per liter. Similarly, with porous electrodes, useful current densities can be achieved with lithium cation concentrations of substantially $10^{-9}$ equivalent per liter, and preferably within the range of from $10^{-2}$ equivalent per liter to $10^{-5}$ equivalent per liter. Accordingly, the saturated concentration of $Li^+$ should be from $10^{-9}$ to $10^{-1}$ equivalent per liter, provided, however, that the saturated concentration of $Li^+$ should always be below the concentration of the supporting electrolyte salt.

The lithium anode metal of the electrochemical
cell of this invention can be used in a variety of
physical forms such as films, powders, compacts of screens,
and can be used alone or in combination with either
conducting or non-conducting substrates.

The positive electrode current collector of the
electrochemical cell can be constructed of any material
which is substantially inert to the cell components.
Preferred materials are metals of the platinum group
family including platinum, iridium, osmium, palladium,
rhodium and ruthenium; carbon in any of its common
electrode forms such as sintered, compacted, powdered
or in rod form and alone or over platinum; iron in various
forms, particularly as stainless stell; and titanium,
nickel, silver, mercury, lead and gold.  Less preferred
materials are metals of the families of vanadium,
chromium and manganese which are selected from Groups
5b, 6b and 7b of the Periodic Table [Handbook of Chemistry
and Physics, 57th ed. (1976-77), p. B-4]; copper, zinc,
cadnium, germanium, tin, antimony and bismuth; certain
nitrides such as boron nitride; and semi-conductors
such as silicon-containing substrates.  All of these
materials can be used in any of the various forms which
are conventional in the art such as rods, compacts,
powders or pastes, for example.

The following examples are intended only to illustrate
the invention and are not to be construed as imposing
limitations thereon.

EXAMPLE 1

The effect of various non-lithium salts on the
solubility in liquid sulfur dioxide of a series of lithium
salts was evaluated in solubility cells which were
constructed from 3.8 cm internal diameter Pyrex® tubing,
which was fused shut at one end and sealed by a Teflon®
gasket to a stainless steel cap at the other end.  A port

was provided in the cap for evacuation, for loading the cell with sulfur dioxide and for removing samples.

High purity sulfur dioxide was purchased commercially in cylinders which had been heated under a vacuum prior to filling in order to minimize any possible contamination by water. The sulfur dioxide was further purified prior to use by storage overnight over strips of lithium metal followed by distillation. The various salts employed were first dried overnight under a vacuum at a temperature in the range of from 100° to 200°C., inclusive.

The cells were loaded with the desired salts in either a nitrogen or an argon filled dry box after which they were sealed, evacuated, and sulfur dioxide was distilled in. The contents were then vigorously stirred for at least 2 hours with a magnetic stirring bar. In each case, the resulting mixture was allowed to settle over-night, and the cell was then weighed. After the resulting solution had been allowed to settle for an additional 4 or 5 hours, a 5 to 15 ml sample thereof was withdrawn into a round-bottomed glass flask, and the solubility cell was then reweighed. Sulfur dioxide was evaporated from the sample under a flow of nitrogen while the sample was heated at a temperature in the range of from 80° to 100°C. The residue in the sample flask was then dissolved with an amount of water in the range of from 25 to 100 grams at a temperature of substantially 90°C. After cooling, the resulting aqueous solution was analysed for lithium by atomic absorption spectroscopy. The Li$^+$ concentration in the sulfur dioxide solution was then calculated; the results are set forth in Tables I, II and III below. The results which are set forth in the columns headed "Obsd." refer to the observed solubilities, and the results in the columns headed " . "Obsd./Calc." were derived by dividing the observed solubility by the calculated solubility. The calculated

solubility used for this purpose was obtained by estimating a solubility product from the lithium salt solubility which was measured in the absence of any additive. All of the solubility measurements were carried out at room tempera-

5    ture (23°C).

The results in Tables I, II and III demonstrates that tetrabutylammonium perchlorate, tetrahexylammonium perchlorate, $Mn(2,2'dipyridyl)_3(ClO_4)_2$ , $Mn(1,10-phenanthroline)_3(ClO_4)_2$, tetramethylammonium

10   tetrafluoroborate, tetrabutylammonium tetrafluoroborate, and tetrapropylammonium hexafluorophosphate are able to exert an enormous effect on the solubility of the corresponding lithium salt having a common anion.  For example, in the case of lithium tetrafluoroborate, the presence of

15   1000 milliequivalents per liter of tetrabutylammonium tetrafluoroborate serves to increase the measured lithium salt solubility by a factor of 220, and this solubility is greater than the calculated value by a factor of one million (see Table II).  It will be appreciated, of course, that

20   the presence of a common anion from another salt would be expected to depress the solubility of a lithium salt.

The data which are set forth in Tables I, II and III also demonstrate that the solubility of lithium salts in sulfur dioxide can be controlled over an extremely large

25   range by the simple expedient of adding a salt which contains at least one cation selected from the group consisting of metal cation complexes and quaternary ammonium cations.  In addition, the results in Tables I, II and III suggest that there is a size-of-cation effect

30   in view  of the diminishing solubility enhancement with cation size for $TBAClO_4$ vs. $THAClO_4$, $TByMnClO_4$ vs. $TPhMnClO_4$, and $TMABF_4$ vs. $TBABF_4$.

EXAMPLE II

A.    Preparation of Supporting Electrolyte Salt.

35   The general procedure for preparing

$Mn(2,2'-dipyridyl)_3(ClO_4)_2$ was the following: 1000 ml of
water were mixed with 1.70g of $MnSO_4 \cdot H_2O$ and 5.00 g of
2,2'-dipyridyl in a 2 liter beaker and heated to 50°C
while stirring.  After all the ingredients had dissolved,

5    5.28g of $LiClO_4$ were added. Stirring was continued
but the heat was turned off.  As crystals began to
form, nitrogen was blown over the solution to inhibit
oxygen contact.  The crystals were allowed to form
until a usable quantity appeared on the bottom of the

10   beaker (typically 1-2 hours).  The
$Mn(2,2'-dipyridyl)_3(ClO_4)_2$ crystals were then filtered
from the solution and dried under a vacuum at 150°C
for 2-4 hours.  [This procedure was adapted from
J. Inorg. Nucl.  Chem. <u>9</u>, 211(1959).]

15        B.    <u>Preparation of Purified SO_2</u>

Sulfur dioxide was purchased commercially in
cylinders which were specially "baked-out" prior to
filing to prevent $H_2O$ contamination.  The sufur dioxide
in gaseous form at 1.2 - 1.4 atm pressure was then

20   passed through evacuated stainless steel tubing and
a system of flow regulators and check valves into the
bottom of a glass column containing glass wool impregnated
with $P_2O_5$.  The $SO_2$ was passed through the glass
wool/$P_2O_5$ and then passed to a receiver tube maintained

25   in an ice bath.  Purified $SO_2$ condensed in the receiver
tube.  Approximately 200 ml of liquid $SO_2$ could be
purified in approximately three hours.  The purifica-
tion system was periodically flushed with argon or
nitrogen and evacuated with a vacuum pump.

30

TABLE I

| Additive Conc.[1] | LiClO$_4$ Solubility[1] (TBAClO$_4$ Additive[2]) | | LiClO$_4$ Solubility[1] (THAClO$_4$ Additive[3]) | |
|---|---|---|---|---|
| | Obsd. | Obsd./Calc. | Obsd. | Obsd./Calc. |
| 0 | 1.4 | | 1.4 | |
| 36 | | | | |
| 130 | | | | |
| 200 | 35 | $10^3$ | 28 | $10^3$ |
| 1000 | > 200 | $10^5$ | | |

| Additive Conc.[1] | LiClO$_4$ Solubility[1] (TByMnClO$_4$ Additive[4]) | |
|---|---|---|
| | Obsd. | Obsd./Calc. |
| 0 | 1.4 | |
| 36 | 18 | $10^2$ |
| 130 | 59 | $10^3$ |
| 200 | | |
| 1000 | | |

(1) Additive concentration and lithium salt solubility are expressed in milliequivalents per liter.

(2) Tetrabutylammonium perchlorate was used as the additive.

(3) Tetrahexylammonium perchlorate was used as the additive.

(4) Mn(2,2'-dipyridyl)$_3$(ClO$_4$)$_2$ was used as the additive.

TABLE II

| | LiClO$_4$ Solubility[1] (TPhMnClO$_4$ Additive[2]) | | LiBF$_4$ Solubility[1] (TMABF$_4$ Additive[3]) | |
|---|---|---|---|---|
| Additive Conc.[1] | Obsd. | Obsd./Calc. | Obsd. | Obsd./Calc. |
| 0 | 1.4 | | 0.2 | |
| 36 | 15 | $10^2$ | | |
| 200 | | | | |
| 500 | | | 12 | $10^5$ |
| 1000 | | | | |

| | LiBF$_4$ Solubility[1] (TBABF$_4$ Additive[4]) | |
|---|---|---|
| Additive Conc.[1] | Obsd. | Obsd./Calc. |
| 0 | 0.2 | |
| 36 | | |
| 200 | 2.3 | $10^4$ |
| 500 | 7 | $10^5$ |
| 1000 | 44 | $10^6$ |

(1) Additive concentration and lithium salt solubility are expressed in milliequivalents per liter.

(2) Mn(1,10-phenanthroline)$_3$(ClO$_4$)$_2$ was used as the additive.

(3) Tetramethylammonium tetrafluoroborate was used as the additive.

(4) Tetrabutylammonium tetrafluoroborate was used as the additive.

TABLE III

| | LiPF$_6$ Solubility[1] (TPAPF$_6$ Additive[2]) | | LiF Solubility[1] (TEAF Additive[3]) |
|---|---|---|---|
| Additive Conc.[1] | Obsd. | Obsd./Calc. | Obsd. |
| 0 | 1.3 | | < 0.1 |
| 500 | 22 | $10^4$ | < 0.1 |
| 1000 | 44 | $10^4$ | |

| | Li$_2$SO$_4$ Solubility[1] (TEASO$_4$ Additive[4]) |
|---|---|
| Additive Conc.[1] | Obsd. |
| 0 | 0 - 0.02 |
| 500 | |
| 1000 | 0.05 - 0.09 |

(1)   Additive concentration and lithium salt solubility are expressed in milliequivalents per liter.

(2)   Tetrapropylammonium hexafluorophosphate was used as an additive.

(3)   Tetraethylammonium fluoride was used as the additive.

(4)   Tetraethylammonium sulfate was used as the additive.

C. Preparation_of_Electrolyte_Solution.

1.83 grams of the solid supporting electrolyte salt
from Step A were placed in a pressurized glass "purifying
cell". 198.5 grams of liquid $SO_2$ in the purifying
5  receiver of Step B were then transferred under pressure
(i.e., at the vapor pressure of $SO_2$ at ambient temperature
to maintain the $SO_2$ at ambient temperature and in the
liquid state) into the purifying cell. The solution in
the  purifying cell was then stirred until all solid
10  material had been dissolved. The purifying cell and
battery cell were connected with the purifying cell
directly above the battery cell; a valve between them
allowed for the transfer of the purifying cell solution
into the battery cell. After being evacuated, the
15  battery cell was filled under pressure from the purifying
cell to a height which just covered the anode foil.

In subsequent Examples, additional lithium salt
or supporting electrolyte salt was placed in the battery
cell prior to filling as noted in Tables V and VII below.
20  It should be noted that the amount of lithium salt and
supporting electrolyte salt actually in the battery cell
during operation was somewhat below the sum of the amounts
added to the purifying and battery cells. Specifically,
Tables V and VII indicate the amounts added to the
25  purifying and battery cells individually, but it should
be emphasized that not all of the $SO_2$ solution in the
purifying cell was transferred to the battery cell.
The actual amount of $SO_2/LiClO_4$ solution transferred
in each Example is also listed in Tables V and VII.

30  D. Cell_Construction_and_Operation

An 1.4 mil lithium foil was used as the anode.
The lithium was supported in a polypropylene holder to
impart rigidity and to protect the electrode from exposure
to the liquid/vapour interface of the cell. In earlier
35  work, it was observed that extensive corrosion of the
foil took place at the liquid/vapour interface. As this

caused mechanical failure in some cases, a polypropylene
holder was devised which simultaneously shielded the
the electrode from contact with the interface and provided
a means of connecting a 40 mil lithium lead-in to the
foil electrode. The cell was filled until the holder
was partially (one-half) submerged. For maximum flexibility,.
three electrodes in total were immersed in the solution:
a lithium foil anode, a carbon reference electrode, and
a porous positive carbon current collector of 15% 30B
Teflon® and 85% Shawinigan Black (60 $m^2$ in surface area).
In Examples III to IX, inclusive, a fourth electrode,
namely, a lithium reference electrode, was also immersed
in the cell solution.

The cell was pressurized at the vapour pressure
of $SO_2$ at ambient temperature. A peculiarity of our
cell design was that the electrode feed throughs at the
top cover of the cell were relatively close together.
We discovered that $SO_2$ condensation on the underside
of the cover sometimes caused shorts between electrodes.
To prevent this condensation, the top cover was heated
to 35°C, but the cell itself and the cell solution were
not heated.

For comparison purposes, the electrolyte of this
cell was prepared without the use of a lithium salt.
One complete cycle comprises a discharge period of approxi-
mately 30 minutes, a 3 minutes period at open circuit,
and a charge period of 30 minutes. Other relevant cell
composition and performance details are contained in
Tables IV and V below.

The following notations were employed in Table IV
and subsequent tables: $Mn(2,2'-dipyridyl)_3(ClO_4)_2$ supporting
electrolyte salt is denoted $TByMnClO_4$;
$Mn(1,10-phenanthroline)_3(ClO_4)_2$ is denoted $TPhMnClO_4$);
the current densities listed are for both the charge
and discharge portions of each cycle; "$LiClO_4$ Sat'n %"
refers to the degree (percentage) of saturation brought
about by the addition of the lithium salt to the electrolyte

solution; and the efficiencies refer to plating efficiencies
based upon the assumption that the only mechanism by
which the amount of available lithium was reduced was
partial irreversibility of discharge product formation.

5          As noted, the cell of Example II had no $LiClO_4$ added
to it.  In operation, the anode of this cell was observed
to deteriorate rapidly; thus, the anode began to corrode
and to dissolve after only a few cycles.  The anode was
almost completely consumed and cell breakdown occurred
10   before one turnover.

                    EXAMPLES III-VI

          The cells were constructed substantially in accord
with the procedures of Example II with the following
exceptions:

15          (1)  An additional purification step was added in
the preparation of purified $SO_2$.  The gaseous $SO_2$ was
first bubbled through a glass column containing glass
wool and $H_2SO_4$ before proceeding to the glass wool/$P_2O_5$
column.  This was intended to help remove any $SO_3$ present.

20          (2)  Lithium perchlorate was added to each cell to
produce increasing $LiClO_4$ concentrations.  Thus, a cell
could be made which was less than 100% saturated in
$LiClO_4$ by adjusting the concentration of a supporting
electrolyte salt which provided additional perchlorate
25   anion.  Specifically, the cell of Example III was first
saturated in $LiClO_4$.  All excess undissolved $LiClO_4$ was
then removed from the cell and sufficient supporting
electrolyte salt was added to bring the $LiClO_4$ concentration
to 30% saturated.  The cell of Example IV was approximately
30   100% saturated, but no solid excess $LiClO_4$ remained in
the bottom of the cell.  Accordingly, while enough $LiClO_4$
was added to the cell of Example IV substantially to
saturate the solution, actual saturation could not be
confirmed with certainty.  Sufficient $LiClO_4$ was added
35   to the cells of Examples V and VI respectively, to produce
an excess of solid $LiClO_4$ in the bottom of the cell.
The actual amounts of supporting electrolyte salt and

$LiClO_4$ placed in the purifying cell and battery cell in
each Example are noted in Table V below.

(3) Each cell was stirred with a magnetic stirrer
during operation.

Composition and performance details are listed in
Tables IV and V below.

### EXAMPLES VII

As regards the preparation of the supporting elec-
trolyte salt, the general procedure for preparing
$Mn(1,10\text{-phenanthroline})_3(ClO_4)_2$ was as follows: 1000 ml
of water were mixed with 1.70g of $MnSO_4 \cdot H_2O$ and 6.00g
of 1,10-phenanthroline·$H_2O$ in a 2-liter beaker and heated
to 50°C with stirring. After all the ingredients had
been dissolved, 2.20g of $LiClO_4$ were added. Stirring
was continued but the heat was turned off. As crystals
began to form, nitrogen was blown over the solution.

The $Mn(1,10\text{-phenanthroline})_3(ClO_4)_2$ crystals were
filtered, collected and dried in a vacuum at 180°C for
2-4 hours. [This procedure was adapted from J. Inorg.
Nucl. Chem. 9, 211 (1959).]

All other aspects of the cell were substantially
identical to Example II. For comparison purposes, no
$LiClO_4$ was added to the electrolyte. Composition and
performance details are contained in Tables VI and VII
below.

### EXAMPLES VIII AND IX

The supporting electrolyte salts were prepared as
in Example VII. All other aspects of Example IX were
prepared in accordance with Examples III-VI.

For Example VIII, however, a solution which was
less than 100% saturated in $LiClO_4$ was prepared substantially
in accord with the method employed in Example III (i.e.,
saturation first, followed by unsaturation through the ad-
dition of supporting electrolyte salt which provided additional
perchlorate anion). Further, an additional $SO_2$ purification
step was performed. After leaving the acid and $P_2O_5$ purifying
columns, the liquid $SO_2$ was routed to a vessel containing
strips of lithium foil and pressurized at the

vapour pressure of $SO_2$ at ambient. The liquid $SO_2$ was
kept in the lithium-containing vessel      at least over-
night prior to use. This step was expected to help
remove any impurities that were reactive with lithium.

Composition and performance details are contained in
Tables VI and VII below.

TABLE IV

| | Example | | | | |
|---|---|---|---|---|---|
| | II | III | IV | V | VI |
| TByMnClO$_4$ Conc., eq/l[1] | 0.036 | 0.13 | 0.042 | 0.056 | 0.048 |
| LiClO$_4$ Conc., eq/l | 0 | 0.018 | 0.018 | 0.018 | 0.018 |
| LiClO$_4$ Sat'n % | 0 | ~ 30 | ~ 100 | 100 | 100 |
| No. of Cycles | 13 | 83 | 210 | 269 | 210 |
| No. of Li Turnovers | < 1 | 3.5 | 9.0 | 11.6 | 10.5 |
| Efficiency, % | - | 71.1 | 88.9 | 91.4 | 90.5 |
| Initial OCV, v | 3.17 | 3.03 | 2.95 | 2.92 | 2.92 |
| Mid-cycle OCV, v | 2.9 | 2.92 | 2.97 | 2.94 | 3.01 |
| Current Density, μA/cm$^2$ | 50 | . 475 | 475 | 475 | 475 |
| 1/2 Cycle Length, min. | 30 | 30 | 30 | 30 | 30 |
| Forming Discharge Length, min. | 3 | 3.3 | 3.6 | 3.7 | 5.3 |
| % Change in Solution Resist. | -9 | +9 | - | - | +8 |

(1)  TByMnClO$_4$ refers to Mn(2,2'-dipyridyl)$_3$(ClO$_4$)$_2$.

TABLE V. Electrolyte Composition

| Electrolyte Component[2] | Example[1] | | | | |
|---|---|---|---|---|---|
| | II | III | IV | V | VI |
| $TByMnClO_4$ | | | | | |
| Total Weight | 1.83 | 2.95 | 1.45 | 1.44 | 1.44 |
| In Purifying Cell | 1.83 | 1.45 | 1.45 | 1.44 | 1.44 |
| In Battery Cell | 0 | 1.50 | 0 | 0 | 0 |
| | | | | | |
| $LiClO_4$ | | | | | |
| Total Weight | 0 | 0.402 | 0.200 | 0.503 | 0.802 |
| In Purifying Cell | 0 | 0.402 | 0.099 | 0.401 | 0.401 |
| In Battery Cell | 0 | 0 | 0.101 | 0.102 | 0.401 |
| | | | | | |
| $SO_2$ | | | | | |
| In Purifying Cell | 198.5 | 125.2 | 132.4 | 101.1 | 117.4 |
| Transferred to Battery Cell | | 66.2 | 70.4 | 58.1 | 75.5 |

(1) The amounts of each electrolyte component are expressed in grams.

(2) $TByMnClO_4$ refers to $Mn(2,2'-dipyridyl)_3(ClO_4)_2$.

## EXAMPLE X

The general procedures for cells employing tetra-n-
butyl ammonium perchlorate (TBAClO$_4$) as the supporting
electrolyte salt were the following:

5          A.    Electrolyte Preparation.

"Electrometric grade" TBAClO$_4$ was purchased commer-
cially and vacuum dried for at least three days.  For two
of the three days, the TBAClO$_4$ was heated over a boiling
water bath.  The dried TBAClO$_4$ was kept stored in an

10    argon glove box.

Lithium perchlorate was dried on a vacuum rack with
a diffusion pump for at least three days at          130°C.
Afterwards, the LiClO$_4$ was kept in an argon glove box.
The moisture content of the TBAClO$_4$ and LiClO$_4$ was mea-

15    sured to be less than 150 ppm.

3.76g TBAClO$_4$ and 0.9g of LiClO$_4$ were placed
in an electrolyte container in the glove box.  The con-
tainer was connected to an SO$_2$ distillation line and
slowly evacuated.  During evacuation, the container was

20    immersed in an isopropanol-dry ice bath and brought to
-50°C.

The line between the container and the SO$_2$ distilla-
tion rack was evacuated.  Gaseous SO$_2$ was then bubbled
through a concentrated H$_2$SO$_4$ bath at less than 1 atm. and

25    routed through a P$_2$O$_5$ drying column and into the electro-
lyte container.  The electrolyte container was brought to,
and maintained at,        -60°C during distillation.  The
SO$_2$ was shut off with        60 ml of SO$_2$ in the electro-
lyte container.  The resulting TBAClO$_4$ concentration was

30        0.18 eq/l.

35

TABLE VI

| | | Example | | |
|---|---|---|---|---|
| | | VII | VIII | IX |
| 5 | TPhMnClO$_4$ Conc., eq/l | 0.038 | 0.14 | 0.038 |
| | LiClO$_4$ Conc., eq/l | 0 | 0.015 | 0.015 |
| | LiClO$_4$ Sat'n % | 0 | ~ 40 | 100 |
| | No. of Cycles | 64 | 78 | 187 |
| | No. of Li Turnovers | < 1 | 3.6 | 8.1 |
| 10 | Efficiency, % | - | 72.3 | 87.6 |
| | Initial OCV, v | 3.07 | 3.01 | 2.91 |
| | Mid-cycle OCV, v | 2.85 | 2.98 | 2.98 |
| | Current Density, $\mu A/cm^2$ | 50 | 475 | 475 |
| 15 | 1/2 Cycle Length, min. | 30 | 30 | 30 |
| | Forming Discharge Length, hrs. | 4.7 | 4.5 | 3.7 |
| | % Change in Solution Resist. | - | -7 | +10 |
| 20 | | | | |

(1) TPhMnClO$_4$ refers to Mn(1,10-phenanthroline)$_3$(ClO$_4$)$_2$.

TABLE VII. Electrolyte Composition

| Electrolyte Component[2] | Example[1] | | |
|---|---|---|---|
| | VII | VIII | IX |
| $TPhMnClO_4$ | | | |
| Total Weight | 2.09 | 3.09 | 1.21 |
| In Purifying Cell | 2.09 | 1.58 | 1.21 |
| In Battery Cell | 0 | 1.51 | 0 |
| $LiClO_4$ | | | |
| Total Weight | 0 | 0.404 | 0.802 |
| In Purifying Cell | 0 | 0.404 | 0.402 |
| In Battery Cell | 0 | 0 | 0.400 |
| $SO_2$ | | | |
| In Purifying Cell | 189.1 | 114.7 | 115.2 |
| Transferred to Battery Cell | | 57.8 | 60.2 |

(1) The amounts of each electrolyte component are expressed in grams.

(2) $TPhMnClO_4$ refers to $Mn(1,10\text{-phenanthroline})_3(ClO_4)_2$.

B.    Electrode Preparation.

Five to ten glass slides were washed scrubbed with
Chem-solv, and thoroughly rinsed.   An 1/2 inch length
of commercial lithium foil was then placed in a molybdenum
container in preparation for vacuum vapour deposition
of a thin lithium film on a clean glass slide.   Deposition
was carried out at $10^{-6}$ mbar vacuum in an Edwards Co.
vacuum deposition apparatus (Model E 306A) for from 30
to 60 minutes.   Obviously, film thickness was dependent
upon deposition time.   The deposition time for each elec-
trode was determined by trial and error; very short times
yielded films that were too thin for good cell performance.
After deposition was complete, the slide was exposed
to a mixture of oxygen and argon for 20 minutes at a
pressure of 0.34 atm.

The resulting glass slide coated with a thin lithium
film was then wrapped at one end with an 0.01 inch thick
lithium ribbon; followed by a nickel ribbon to act as
a tab connector.   The slide was then dipped in wax until
both ends were covered with wax, leaving exposed a
rectangle of lithium film 1.5 x 2.5 cm in size.

C.    Cell Assembly.

It should be stressed .that cleanliness was essential.
Clean, dry latex gloves (washed well with soap and water
and rinsed with ethanol) and filter masks were used at
all times in assembling the cell and handling the glass
slide anode.   Care was also taken to avoid cross contamina-
tion due to unclean tools or improper washing. All
assembly was performed in a dry·room (less than 1% relative
humidity).

The lithium anode, carbon current collector and any
reference electrodes that were used were inserted into
stainless steel feed throughs in the polypropylene top
of a glass cell cylinder.   A stainless steel fill tube
extended through the top of the cell to beneath the elec-
trolyte level.   The electrolyte container and cell were
then connected, and the connecting line between them was

repeatedly evacuated and flushed with argon. The valve
between the electrolyte container and the cell was slowly
opened to transfer the electrolyte into the cell. When
all of the exposed portion of the lithium film on the

5       anode was covered with electrolyte, the filing was com-
plete.

        It should be noted that no stirring of the electrolyte
or cell was effected in order to dissolve the $LiClO_4$ salt.
In this example, two lithium electrodes on glass slides

10      were prepared simultaneously. The $SO_2$/$TBAClO_4$ electrolyte
was prepared 3 days prior to use. During operation, both
lithium electrodes and a carbon (15% Teflon ® 7C, 85%
Shawinigan Black) electrode were inserted into the elec-
trolyte. The cell was then cycled through numerous

15      charge discharge cycles with each lithium electrode being
cycled versus the other lithium electrode. The carbon
electrode was used only as a reference electrode against
which the open circuit voltage (OCV) measurements were
taken.

20      Composition and performance details of this cell
are contained in Table VIII below. The same assumption
and definitions regarding efficiency and turnovers made
in Tables IV and VI also pertain to Table VIII.

        EXAMPLE XI

25      The cell components were prepared in accord with the
method of Example X. 4.1g of $TBAClO_4$ and 0.32g of $LiClO_4$
were added to 60 ml of $SO_2$ to form the electrolyte in the
electrolyte container. 0.5g of additional $LiClO_4$ was
added to the battery cell prior to filling. Sufficient

30      $LiClO_4$ was present in the cell substantially to saturate
the cell solution. The electrolyte was mechanically
stirred for 63 hours prior to filing the cell, but the
cell itself was not stirred after filing. One lithium
anode on glass and two carbon electrodes were inserted into

35      the cell. All cycling was done between the lithium anode

and a carbon current collector. After 246 cycles, the
cell failed from deterioration of the lithium anode.
Composition and performance details are summarized in
Table VIII below.

5 EXAMPLE XII

The cell components were prepared in accord
with the method of Example X.  6.84g of $TBAClO_4$ and 1.5g
of $LiClO_4$ were added to 100 ml of $SO_2$ in the electrolyte
container to form the electrolyte.  No additional $LiClO_4$
10 was added to the cell.  Sufficient $LiClO_4$ was present
in the cell substantially to saturate the cell solution.
The electrolyte was ultrasonically stirred for 1 hour
prior to filing the cell and the ultrasonic stirring
was continued during cycling.  To compensate for heating
15 effects caused by the ultrasonic stirring, the cell was
maintained in a cooling bath at 20°C.  All cycling was
performed between the lithium anode and a carbon current
collector.  After 456 cycles, the cell failed from
deterioration of the anode.  Composition and performance
20 details are summarized in Table VIII below.

EXAMPLE XIII

The cell components were prepared in accord
with the method of Example X.  2.73g of $TBAClO_4$ and O.11g
of $LiClO_4$ were added to 40 ml of $SO_2$ in the electrolyte
25 container to form the electrolyte.  No additional $LiClO_4$
was added to the cell.  For comparison purposes, the
quantity of $LiClO_4$ present was not sufficient to saturate
the cell solution.  The electrolyte was mechanically
stirred for 20 hours prior to filling the cell; the cell
30 itself was not stirred after filling.  All cycles were
performed between the lithium anode and a carbon current
collector.  As expected, the unsaturated electrolyte
performed poorly; the cell failed due to deterioration
of the anode after 104 cycles (less than one turnover).
35 Composition and performance details are summarized in

Table VIII below.

Some observations are noteworth. In general, cells unsaturated in lithium perchlorate failed more rapidly than saturated cells although some cycling was accomplished. In addition, it appears that the cells of Examples XI and XII did not perform as well as the cell of Example X, although all three were substantially saturated in $LiClO_4$.

The lower performance of Examples XI and XII is believed to be due to the presence of water. Measurements performed after the cell had failed indicated that the $LiClO_4$ used in these cells contained 274 ppm of $H_2O$. This water, when combined with estimates of the water content of the $TBAClO_4$ and $SO_2$, yields an estimate of $2.5 \times 10^{-5}$ moles of $H_2O$ in the electrolyte. As lithium electrode typically contained $4 \times 10^{-5}$ moles of lithium, a water content as high as $10^{-5}$ moles could have caused a significant loss of lithium from the surface of the anode.

In addition, as previously noted, increasing the concentration of the perchlorate supporting electrolyte salt served to increase the saturated concentration of the lithium perchlorate. As both salts have the same anion, this result is anomalous and is not fully understood. Nevertheless, this effect can be utilized to adjust the solubility of the lithium perchlorate. In short, it is possible to adjust the saturated concentration of the lithium perchlorate through an adjustment of the perchlorate supporting electrolyte salt concentration.

TABLE VIII

| | | Example | | | |
|---|---|---|---|---|---|
| | | X | XI | XII | XIII |
| 5 | TBAClO$_4$ Conc., eq/l[1] | 0.18 | 0.20 | 0.20 | 0.20 |
| | LiClO$_4$ Conc., eq/l | 0.035 | 0.035 | 0.035 | 0.025 |
| | LiClO$_4$ Sat'n % | 100 | 100 | 100 | ~ 70 |
| | No. of Cycles | 1,785 | 246 | 456 | 104 |
| | No. of Li Turnovers | ~ 30 | 2.73 | 2.98 | 0.85 |
| 10 | Efficiency, % | 97.2 | 81.9 | 83.2 | 40.8 |
| | Initial OCV, v | 3.11 | 3.02 | 2.99 | 2.99 |
| | Mid-Test OCV, v | 3.15 | 3.27 | 3.03 | None |
| | (after No. cycles) | (836) | (127) | (260) | |
| | Current Density, $\mu$A/cm$^2$ | ~ 12 | 14 | 14 | 11 |
| 15 | 1/2 Cycle Length, min. | 10 | 10 | 10 | 10 |
| | Forming Discharge Length, min. | 20 | 20 | 20 | 20 |
| | Stirred: | | | | |
| | Electrolyte | No | Yes | Yes | Yes |
| 20 | Cell | No | No | Yes | No |

(1) TBAClO$_4$ refers to tetrabutylammonium perchlorate.

CLAIMS

1.      A method of modifying the solubility of a
lithium salt in a non-aqueous solvent system which compri-
ses dissolving the lithium salt and a solubility-modifying
additive in the solvent system, characterised in that
said solvent system comprises a major proportion of sulfur
dioxide; in that the amount of said lithium salt is in
excess of the amount which is soluble in the solvent
system in the absence of said solubility-modifying additive,
the amount of said solubility-modifying additive being
effective to increase the solubility of said lithium salt; and
in that said solubility-modifying additive comprises ·
a  salt which contains at least one cation selected from
the group consisting of metal cation complexes, quaternary
ammonium cations and organic phosphonium cations.

2.      A method as set forth in Claim 1, further
characterised in that the amount of said lithium salt
is effective substantially to saturate the solvent system
in the presence of said solubility-modifying additive.

3.      A method as set forth in Claim 1, further
characterised in that the amount of said solubility-
modifying additive is effective at least to double the
solubility of said lithium salt.

4.      A method as set forth in Claim 1, further
characterised in that said solvent system is substantially
pure sulfur dioxide.

5.      A method as set forth in Claim 1, further
characterised in that said solubility-modifying additive
has a solubility in said solvent system at the temperature
and pressure of use of at least 0.1 equivalent per liter.

6.      A method as set forth in Claim 1, further
characterised in that said lithium salt and said solubility-
modifying additive contain a common anion.


7.      A method as set forth in Claim 1, further
characterised in that said cation is selected from the
group consisting of $Mn(2,2'\text{-dipyridyl})_3^{++}$ and
$Mn(1,10\text{-phenanthroline})_3^{++}$.


8.      A method as set forth in Claim 1, further
characterised in that said solubility-modifying additive
is a quaternary ammonium salt of the formula:

$$R^1 \text{———} N^+ \text{———} R^3 \qquad X^-$$

with $R^2$ above and $R^4$ below the nitrogen.
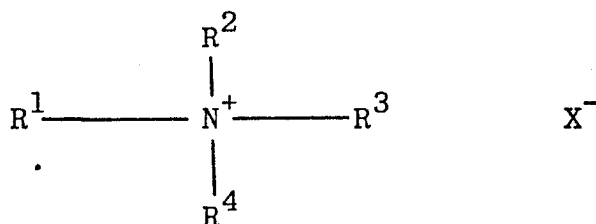
wherein $R^1$, $R^2$, $R^3$ and $R^4$ are independently selected
from the group consisting of hydrocarbyl groups of from
1 to 20 carbon atoms, and $X^-$ is selected from the group
consisting of perchlorate, .tetrafluoroborate, hexafluoro-
phosphate, dithionite, sulfate, phosphate, chloride,
bromide, iodide and fluoride.


9.      A method as set forth in Claim 8, further
characterised in that $R^1$, $R^2$, $R^3$ and $R^4$ are independently
selected from the group consisting of alkyl groups of
from 1 to 10 carbon atoms, and $X^-$ is selected from the
group consisting of perchlorate, tetrafluoroborate,
hexafluorophosphate, dithionite and sulfate.


10.     A method as set forth in Claim 1, further
characterised in that said solubility-modifying additive
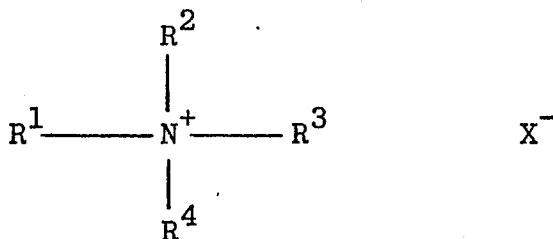is a phosphonium salt of the formula:

$$R^1 \underline{\hspace{1cm}} \overset{\displaystyle R^2}{\underset{\displaystyle R^4}{\overset{|}{\underset{|}{P^+}}}} \underline{\hspace{1cm}} R^3 \qquad\qquad X^-$$
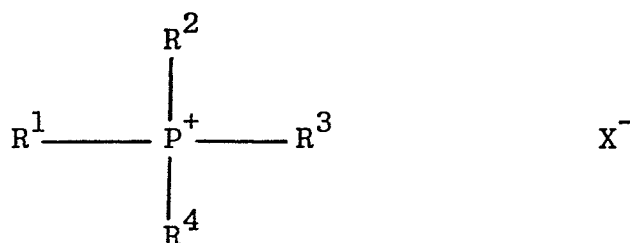
wherein $R^1$, $R^2$, $R^3$ and $R^4$ are independently selected from the group consisting of hydrocarbyl groups containing from 1 to 20 carbon atoms, and $X^-$ is selected from the group consisting of perchlorate, tetrafluoroborate, hexafluorophosphate, dithionite, sulfate, phosphate, chloride, bromide, iodide and fluoride.

11.     A method as set forth in Claim 1, further characterised in that said lithium salt is selected from the group consisting of lithium perchlorate, lithium dithionite, lithium sulfate, lithium tetrafluoroborate. and lithium hexafluorophosphate.

12.     The composition prepared by the process which comprises dissolving a lithium salt and a solubility-modifying additive in a non-aqueous solvent system, characterised in that said solvent system comprises a major proportion of sulfur dioxide, in that the amount of said lithium salt is in excess of the amount which is soluble in the solvent system in the absence of said solubility-modifying additive, the amount of said solubility-modifying additive being effective to increase the solubility of said lithium salt; and in that said solubility-modifying additive comprises a salt which contains at least one cation selected from the group consisting of metal cation complexes, quaternary ammonium cations and organic phosphonium cations.

13.     A composition as set forth in Claim 12, further
characterised in that the amount of said lithium salt
is effective substantially to saturate the solvent
system in the presence of said solubility-modifying
additive.

14.     A composition as set forth in Claim 12, further
characterised in that the amount of said solubility-
modifying additive is effective to at least double
the solubility of said lithium salt.

15.     A composition as set forth in Claim 12, further
characterised in that said solvent system is substantially
pure sulfur dioxide.

16.     A composition as set forth in Claim 12, further
characterised in that said cation is selected from
the group consisting of $Mn(2,2'-dipyridyl)_3^{++}$ and
$Mn(1,10-phenanthroline)_3^{++}$.

17.     A composition as set forth in Claim 12, further
characterised in that said solubility-modifying additive
is a quaternary ammonium salt of the formula:

$$R^1 \underset{\underset{R^4}{\displaystyle |}}{\overset{\overset{R^2}{\displaystyle |}}{\displaystyle N^+}} R^3 \qquad X^-$$

wherein $R^1$, $R^2$, $R^3$ and $R^4$ are independently selected
from the group consisting of hydrocarbyl groups of
from 1 to 20 carbon atoms, and $X^-$ is selected from
the group consisting of perchlorate, tetrafluoroborate,
hexafluorophosphate, dithionite, sulfate, phosphate,
chloride, bromide, iodide and fluoride.

18.     A composition as set for in Claim 12, further characterised in that said solubility-modifying additive is a phosphonium salt of the formula:

$$R^1 \underset{\overset{\displaystyle |}{R^4}}{\overset{\overset{\displaystyle R^2}{\displaystyle |}}{P^+}} R^3 \qquad X^-$$
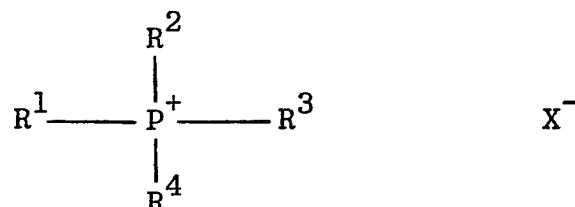
wherein $R^1$, $R^2$, $R^3$ and $R^4$ are independently selected from the group consisting of hydrocarbyl groups containing from 1 to 20 carbon atoms, and $X^-$ is selected from the group consisting of perchlorate, tetrafluoroborate, hexafluorophosphate, dithionite, sulfate, phosphate, chloride, bromide, iodide and fluoride.

19.     A composition as set forth in Claim 12, further characterised in that said lithium salt is selected from the group consisting of lithium perchlorate, lithium dithionite, lithium tetrafluoroborate and lithium hexafluorophosphate.

20.     An electrochemical cell characterised by
(a)     a lithium anode;
(b)     a positive electrode current collector; and
(c)     an electrolyte which comprises a composition according to any of Claims 12 to 19.